ANALYSIS AND APPLICATIONS: BINARY PHASE DIAGRAMS

7.1 EUTECTIC SYSTEMS: NO SOLID SOLUBILITY

Computation of thermodynamic properties of solutions from phase diagrams is now quite common although the complexities of the techniques described in the literature, particularly ternary systems, do not lend themselves easily to practical applications. The thermodynamic loop can be readily applied to phase diagram analysis. The TL is first superimposed directly around the equilibrium line of interest on the diagram (personal communication, 1959, R. Schuhmann, Jr., Department of Metallurgical Engineering, Purdue University, West Lafayette, Indiana). Various solution models are then tested to complete the analysis. In this chapter, the solution models used for analysis are ideal, regular, and dilute. Examples for eutectic systems with no solid solubility and terminal solubility are presented in this and subsequent sections. The chapter concludes with discussion of the Gibbs Phase rule.

As defined in Chapter 6, the parameters associated with $\bar{H}^m$ and $\bar{S}^m$ are independent of temperature. Temperature-composition data obtained directly from phase diagrams is correlated with thermodynamic expressions for liquidus, solidus, and solvus curves. Since fusion is incorporated into the analysis, a choice can be made whether or not to assume $\Delta C_p = 0$ for conversion of standard states from solid to liquid.

Consider the A-B alloy in Figure 7.1 for which the liquidus is thermodynamically characterized by the TL: $1 \rightarrow 2 \rightarrow 3 \rightarrow 4 \rightarrow 1$.
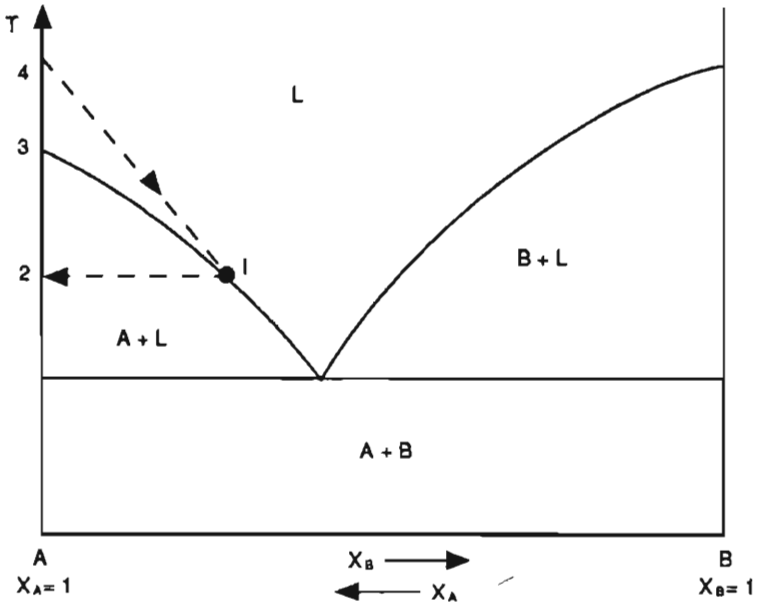
Figure 7.1 Temperature-composition eutectic phase diagram for components A and B with no solid solubility.

The following notation is used with reference to Figure 7.1:

Point	Phase Designation	Gibbs Free Energy
1	$\overline{A}$ (l) (Component A in liquid solution)	$\overline{G}_A^l$
2	$A^0(s)$ (Solid A)	$G_A^{0,s}$
3	$A^0(s) \rightarrow A^0(l)$ (Fusion of Solid A)	$G_A^{0,l} - G_A^{0,s}$
4	$A^0(l)$ (Liquid A)	$G_A^{0,l}$

Characterizing the thermodynamic loop:

Process	Reaction	Gibbs Free Energy Change
$1 \to 2$	$\overline{A}(l) \to A^0(s)$	$G_A^{0,s} - \overline{G}_A^l = 0.$ Solid A in equilibrium with A in liquid solution (from the diagram).
$2 \to 3 \to 4$	$A^0(s) \to A^0(l)$	$G_A^{0,l} - G_A^{0,s} = \Delta H_A^f +$ $\int_{T^f}^T \Delta C_p^A dT - T\left[\Delta S_A^f + \int_{T^f}^T (\Delta C_p^A / T)dT \right]$ where ΔH_A^f and ΔS_A^f are heat and entropy of fusion respectively and $\Delta C_p^A = C_p^{A(l)} - C_p^{A(s)}$.
$4 \to 1$	$A^0(l) \to \overline{A}(l)$	$\overline{G}_A^l - G_A^{0,l} = \overline{G}_A^{m,l} = \overline{H}_A^{m,l} - T\overline{S}_A^{m,l}.$

Summing about the TL in Figure 7.1,

$$\Sigma \Delta G_{TL} = 0 = \Delta H_A^f + \int_{T^f}^T \Delta C_p^A dT - T\left[\Delta S_A^f + \int_{T^f}^T (\Delta C_p^A / T)dT \right] + \overline{H}_A^{m,l} - T\overline{S}_A^{m,l}.$$

Solving for T, the liquidus is given by

$$T = \frac{\overline{H}_A^{m,l} + \Delta H_A^f + \int_{T^f}^T \Delta C_p^A dT}{\overline{S}_A^{m,l} + \Delta S_A^f + \int_{T^f}^T \frac{\Delta C_p^A dT}{T}} \qquad [7\text{-}1]$$

For the specific case where $\Delta C_p^A \approx 0$,

$$T = \frac{\overline{H}_A^{m,l} + \Delta H_A^f}{\overline{S}_A^{m,l} + \Delta S_A^f} = \frac{\Sigma \Delta H}{\Sigma \Delta S} \qquad [7\text{-}2]$$

In general, temperature is equal to the sum of enthalpy terms divided by the sum of entropy terms. In order to relate [7-1] or [7-2] to the phase diagram, solution models are incorporated as follows:

Using [7-2]:
(1) Ideal Solution: substituting [6-27] and [6-28],

$$T = \frac{\Delta H_A^f}{-R \ln(X_A) + \Delta S_A^f} \qquad [7\text{-}3]$$

(2) **Dilute Solution:** substituting [6-35] and [6-36],

$$T = \frac{h + \Delta H_A^f}{s - R \ln(X_A) + \Delta S_A^f} \qquad [7\text{-}4]$$

(3) **Regular Solution:** substituting [6-39] and [6-42],

$$T = \frac{\Omega(1 - X_A)^2 + \Delta H_A^f}{-R \ln(X_A) + \Delta S_A^f} \qquad [7\text{-}5]$$

Example problems below illustrate the analysis of liquidus curves using trial and error combinations of [7-3], [7-4], and [7-5].

Example Problem 7-1

Analyze ideal and regular solution models for the Si liquidus of the Al-Si phase diagram. Plot the results for comparison on Figure E.6 in Appendix E.

Solution

From Table A.2, ΔH_{Si}^f = 50,630 J/mol at T_{Si}^f = 1693 K.* From [4-8] at the melting point, $\Delta G_{1693}^f = 0 = \Delta H_{1693}^f - 1693 \Delta S_{1693}^f$. Hence, ΔS_{1693}^f = 50,630/1693 = 29.91 J/(mol·K).

Test (1): *Ideal Solution Model.* Applying [7-3],

$$T\,(K) = \frac{50,630}{-8.3144 \ln(X_{Si}) + 29.91}.$$

Selecting concentrations from X_{Si} = 1.0 to X_{Si} = 0.122 at the eutectic temperature, the liquidus temperature is calculated and tabulated in Table 7.1:

Table 7.1
Calculated Si Liquidus: Al-Si System—Ideal Solution Model
$T(K) = 50,630/[-8.3144\ln(X_{Si}) + 29.91]$

X_{Si}	T (K)	T (°C)
1.0	1693	1420
0.9	1645	1372
0.7	1540	1267
0.5	1419	1146
0.3	1268	995
0.122	1068	795

A plot of the data from Table 7.1 onto Figure E.6 reveals increasing deviation from the experimentally derived liquidus as X_{Si} decreases. As expected, the behavior of Si tends to be ideal at concentrations approaching X_{Si}=1.0.

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* Use 1693 K for consistency with the equilibrium diagram.

Test (2): *Regular Solution Model.* Applying [7-5],

$$T \text{ (K)} = \frac{\Omega^l(1 - X_{Si})^2 + 50,630}{-8.3144 \ln(X_{Si}) + 29.91} \qquad [7\text{-}6]$$

The problem becomes one of finding a value for Ω^l that provides a reasonable fit to the liquidus curve. If such a value can be found, the solution tends to be regular. From [7-6],

$$\Omega^l = \{T[29.91 - 8.3144 \ln(X_{Si})] - 50,630\}/(1 - X_{Si})^2.$$

Selecting concentrations, X_{Si}, and corresponding T from the liquidus, Ω^l is calculated and tabulated in Table 7.2. Data from the literature is also included.

Table 7.2

Calculated Ω^l and $\overline{H}_{Si}^m$ from the Si Liquidus: Al-Si System— Regular Solution Model

$$\Omega^l = \{T[29.91 - 8.3144 \ln(X_{Si})] - 50,630\}/(1 - X_{Si})^2$$

X_{Si}	T(K)		Ω^l (J/mol) Calculated	$\overline{H}_{Si}^m$ (J/mol)= $\Omega^l_{Ave}(1-X_{Si})^2$ Calculated[a]
1.0	1687		$-\infty$	≈ 0[b]
0.9	1628		$-51,038$	≈ 0[b]
0.7	1513		-9881	-1104
				(-1406)
0.5	1333	$\Omega^l_{Ave.}=$	$-12,311$	-3067
				(-3598)
0.3	1103	$-12,267$	$-13,465$	-6011
				(-6276)
0.122	850		$-13,412$	-9456

(a) Non-parenthetical values are calculated using $\Omega^l_{Average} = -12,267$ J/mol. Parenthetical values are from Kubaschewski and Alcock, 1979, p. 389-90. The data from Kubaschewski and Alcock includes excess entropy whereas the regular solution does not. This may explain the difference between calculated and published values of $\overline{H}_{Si}^m$.
(b) At approximately $X_{Si} > 0.9$, $\overline{H}_{Si}^m \approx 0$ since the solution is virtually ideal with respect to Si(l) in this range. Note that the calculation for Ω^l is invalid at $X_{Si} = 1.0$.

Temperature is calculated as a function of composition from [7-6] using $\Omega^l_{Average}$ and tabulated in Table 7.3. A plot of the data from this table onto

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Table 7.3

Calculated Si Liquidus: Al-Si System—Regular Solution Model

$T(K) = [-12,267(1 - X_{Si})^2 + 50,630]/[-8.3144\ln(X_{Si}) + 29.91]$

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| X_{Si}	T (K) (Calculated)	T (K) (Phase Diagram)
1.0	1693	1687
0.9	1641	1628
0.7	1506	1513
0.5	1333	1333
0.3	1118	1103
0.122	869	850

Figure E.6 reveals good correlation with the experimentally derived liquidus for a regular solution between the eutectic composition and $X_{Si} \approx 0.9$. Deviation from ideality is negative, therefore, mixing is exothermic. From [6-40], unlike pairs of atoms attract.

Example Problem 7-2

Calculate the equilibrium partial pressure of $N_2(g)$ over a eutectic liquid solution of Al-Si at the eutectic temperature. Assume $Si_3N_4(s)$ is a reaction product insoluble in the liquid solution. What is the limiting P_{N_2} below which $Si_3N_4(s)$ is reduced?

Solution

(1) Set Up.
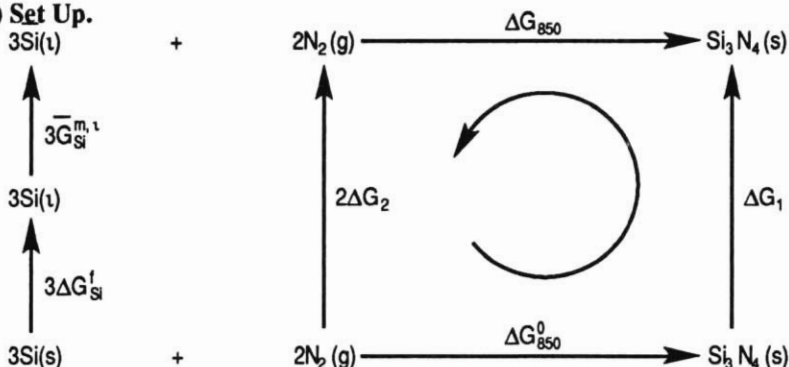
Note that the fusion of Si must be incorporated into the loop since Si is dissolved as a liquid in solution. In addition, $\overline{G}_{Si}^{m,l}$ is defined with respect to pure liquid Si according to [6-14].

(2) Sum.

$$\Sigma \Delta G_{TL} = 0 = \Delta G_{850}^0 + \Delta G_1 - \Delta G_{850} - 2\Delta G_2 - 3\overline{G}_{Si}^{m,l} - 3\Delta G_{Si}^f.$$

(3) Substitute.

$\Delta G_{850}^0 = -753,190 + 336.43T$ from Table A.4. From the Al-Si phase diagram, Figure E.6, the eutectic temperature $T_e = 850$ K, hence

$\Delta G_{850}^0 = -753,190 + 336.43(850) = -467,225$ J/mol.

$\Delta G_1 = 0.$

$\Delta G_{850} = 0$ (equilibrium).

$2\Delta G_2 = 2(8.3144)(850)\ln (P_{N_2}).$

Using the data in Example Problem 4-6 and assuming $\Delta C_p \approx 0$, the Gibbs free energy of fusion of Si(s) at 850 K is

$3\Delta G_{Si}^f = 3[50,630 - 850(29.91)] = 75,620$ J/mol.

From Example Problem 7-1, $\Omega^l = -12,267$ J/mol and at the eutectic temperature $T_e = 850$ K, $X_{Si} = 0.122$. Substituting into [6-43],

$$3\overline{G}_{Si}^{m,l} = 3\left(\overline{H}_{Si}^{m,l} - T_e\overline{S}_{Si}^{m,l}\right) = 3\left\{\Omega^l(1 - X_{Si})^2 - T_e\left[-R\ln(X_{Si})\right]\right\}$$

$$= 3\left\{-12,267(1 - 0.122)^2 - 850[-8.3144\ln(0.122)]\right\}$$

$$= -72,972 \text{ J/mol.}$$

Substituting into $\Sigma \Delta G_{TL} = 0$,

$0 = -467,225 - 2(8.3144)(850)\ln (P_{N_2}) - (-72,972) - 75,620.$

(4) Solve.

$P_{N_2} = \underline{3.7 \times 10^{-15}}$ atm. This is the limiting P_{N_2} below which $Si_3N_4(s)$ tends to be reduced.

Example Problem 7-3

The solubility of iron in liquid lithium is 0.35 w/o at 1200°C and 0.004 w/o at 400°C. Given this information, (a) Estimate the maximum purity of liquid lithium with respect to iron that can be obtained by slowly cooling a high Li-Fe liquid solution. The eutectic temperature is only a fraction of a degree lower than the melting point of pure lithium; thus, the problem involves the calculation of the solubility of iron at the lowest temperature at which the solution is a liquid. For practical purposes, this temperature is the melting point of lithium. (b) Estimate the eutectic temperature and composition of the high Li-Fe liquid solution.

Solution

(a) At low concentration (< approximately 1 a/o solute) the solution is dilute

with respect to iron solute, hence the solution model is characterized by [7-4]. A phase diagram is sketched in Figure 7.2 to illustrate the problem. Substituting ΔH_{Fe}^f and ΔS_{Fe}^f from Table A.2 into [7-4],

$$T = \frac{h_{Fe}^l + 13,770}{s_{Fe}^l - R\ln(X_{Fe}^l) + 7.6119} \qquad [7\text{-}7]$$

Since $X_{Fe}^l = (a/o)/100$, the solubility must be converted from w/o to atomic fraction. From [6-5a],

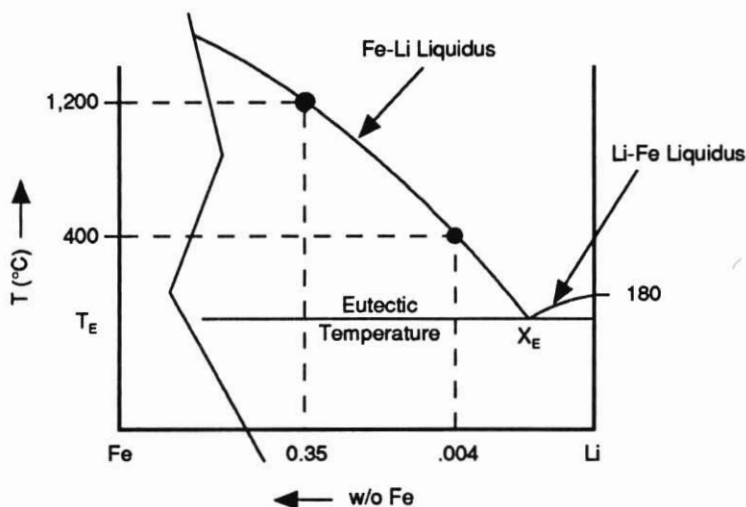$$X_{Fe} = \frac{w/o|_{Fe}/55.85}{\left(w/o|_{Fe}/55.85\right) + \left(w/o|_{Li}/6.94\right)}.$$

Figure 7.2 Partial temperature-composition phase diagram (not to scale): high lithium-iron eutectic, no solid solubility.

From the given data:
$X_{Fe} = 4.36 \times 10^{-4}$ at 0.35 w/o Fe and 1473 K;
$X_{Fe} = 4.97 \times 10^{-6}$ at 0.004 w/o Fe and 673 K.
Substituting and solving [7-7] simultaneously for two unknowns:

$$1473 = \frac{h_{Fe}^l + 13,770}{s_{Fe}^l - 8.3144\ln(4.36 \times 10^{-4}) + 7.6119};$$

$$673 = \frac{h_{Fe}^l + 13,770}{s_{Fe}^l - 8.3144\ln(4.97 \times 10^{-6}) + 7.6119}$$

hence,
$$h_{Fe}^l = 32,331 \text{ J/mol};$$
$$s_{Fe}^l = -40.65 \text{ J/(mol·K)}.$$

Inserting these values into [7-7] and collecting terms:

$$T = \frac{46,101}{-33.038 - 8.3144 \ln(X_{Fe}^l)} \qquad [7\text{-}8]$$

The minimum iron content in lithium at the melting point of lithium (453 K) is estimated to be

$$\ln(X_{Fe}^l) = \frac{46,101 + 33.038T}{-8.3144T}$$

$$= \frac{46,101 + 33.038(453)}{-8.3144(453)}$$

or

From [6-5b], $\qquad X_{Fe}^l = 9.089 \times 10^{-8} \sim 0.7 \text{ ppm}.$

(b) In Example Problem 6-8, it was shown if the solute is dilute, the solvent is ideal. Substituting $\Delta H_{Li}^f = 2929$ J/mol and $\Delta T_{Li}^f = 453$ K into [7-3],

$$T = \frac{2929}{-8.3144 \ln(X_{Li}) + 2929/453} \qquad [7\text{-}9]$$

Solving [7-8] and [7-9] simultaneously for T_e (eutectic temperature) and X_e (eutectic composition):

$$T_e = \frac{46,101}{-33.038 - 8.3144 \ln\left(X_e\right)};$$

$$T_e = \frac{2929}{-8.3144 \ln\left(1 - X_e\right) + 6.466}$$

where

$$X_e = X_{Fe} \text{ and } 1 - X_e = X_{Li}$$

hence,

$$X_e = 9.083 \times 10^{-8};$$
$$T_e = 452.9 \text{ K}(179.9\,°C).$$

Example Problem 7-4

The solubility of carbon in liquid aluminum is 6 ppm at 960°C and 12.5 ppm at 1000°C.* Predict the solubility at the melting point of Al, 660°C. Assume dilute behavior.

Solution

Since carbon as graphite does not have a known fusion temperature, use pure

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* According to Simensen (1989, p. 191), Al-C melts are saturated with carbon and also contain traces of carbides (Al_4C_3).

solid C as the standard state. As a result, fusion terms in [7-4], are dropped and

$$T = \frac{h}{s - R\ln(X_C)} \qquad [7\text{-}10]$$

Converting solubility data to atomic fraction,

At 960°C:
$$X_C = \frac{6/12}{6/12 + \approx 10^6/26.984}$$
$$= 13.49 \times 10^{-6} \approx 6 \text{ ppm}.$$

At 1000°C:
$$X_C = \frac{12.5/12}{12.5/12 + \approx 10^6/26.984}$$
$$= 28.11 \times 10^{-6} \approx 12.5 \text{ ppm}.$$

Substituting into [7-10],
$$1233 = h_C/[s - 8.3144\ln(13.49 \times 10^{-6})];$$
$$1273 = h_C/[s - 8.3144\ln(28.11 \times 10^{-6})].$$

Solving simultaneously,
$$h_C = 239{,}490 \text{ J/mol};$$
$$s_C = 101 \text{ J/(mol·K)}.$$

Substituting h_C, s_C, and $T = 660°C$ (993 K) into [7-10] and solving for X_C, From [6-5b], $\qquad X_C = 7.38 \times 10^{-9} \approx 3$ ppb .

7.2 EUTECTIC SYSTEMS: TERMINAL SOLID SOLUBILITY

Consider the A-B alloy in Figure 7.3 for which the liquidus and solidus are thermodynamically characterized by the TL: $1 \rightarrow 2 \rightarrow 3 \rightarrow 4 \rightarrow 5 \rightarrow 1$.
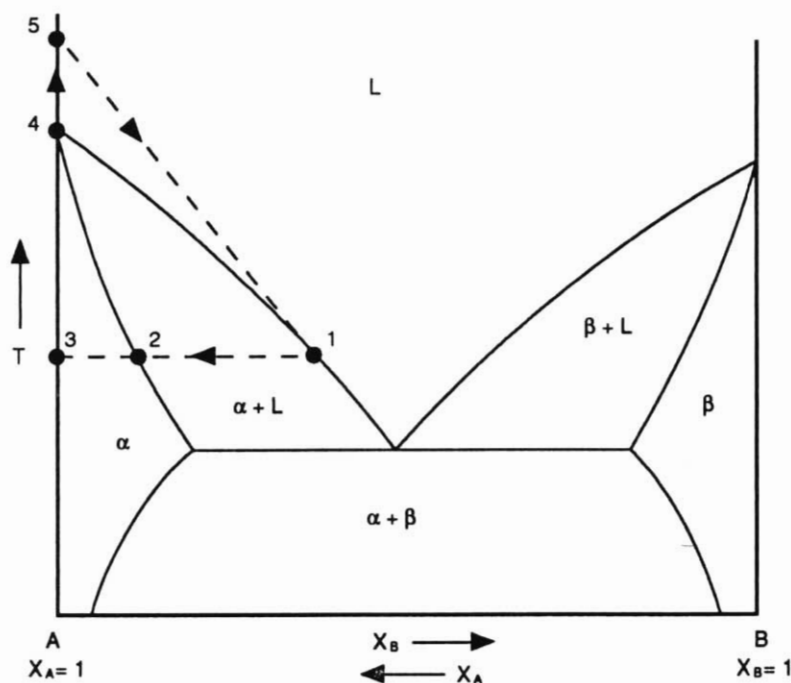

Figure 7.3 Temperature-composition eutectic phase diagram for components A and B with terminal solid solubility.

The following notation is used with reference to Figure 7.3:

Point	Phase Designation	Gibbs Free Energy
1	$\overline{A}(l)$ (Component A in liquid solution)	$\overline{G}_A^l$
2	$\overline{A}(\alpha)$ (Component A in α solid solution)	$\overline{G}_A^\alpha$
3	$A^0(s)$ (Solid A)	$G_A^{0,s}$
4	$A^0(s) \rightarrow A^0(l)$ (Fusion of Solid A)	$G_A^{0,l} - G_A^{0,s}$
5	$A^0(l)$ (Liquid A)	$G_A^{0,l}$

Characterizing the thermodynamic loop:

Process	Reaction	Gibbs Free Energy Change
$1 \rightarrow 2$	$\overline{A}(l) \rightarrow \overline{A}(\alpha)$	$\overline{G}_A^\alpha - \overline{G}_A^l = 0$
$2 \rightarrow 3$	$\overline{A}(\alpha) \rightarrow A^\circ(s)$	$G_A^{0,s} - \overline{G}_A^\alpha = -\overline{G}_A^{m,\alpha}$
		where $-\overline{G}_A^{m,\alpha} = -\overline{H}_A^{m,\alpha} + T\overline{S}_A^{m,\alpha}$
$3 \rightarrow 4 \rightarrow 5$	$A^0(s) \rightarrow A^0(l)$	$G_A^{0,l} - G_A^{0,s} = \Delta H_A^f - T\Delta S_A^f$
$5 \rightarrow 1$	$A^0(l) \rightarrow \overline{A}(l)$	$\overline{G}_A^l - G_A^{0,l} = \overline{G}_A^{m,l}$
		where $\overline{G}_A^{m,l} = \overline{H}_A^{m,l} - T\overline{S}_A^{m,l}$

Summing about the TL in Figure 7.3,
$$\Sigma \Delta G_{TL} = 0 = 0 - \overline{H}_A^{m,\alpha} + T\overline{S}_A^{m,\alpha} + \Delta H_A^f - T\Delta S_A^f + \overline{H}_A^{m,l} - T\overline{S}_A^{m,l}.$$
Solving for T and assuming $\Delta C_p^A = C_p^{A(l)} - C_p^{A(\circ)} \approx 0$, the equation for the liquidus* is:

$$T = \frac{\overline{H}_A^{m,l} - \overline{H}_A^{m,\alpha} + \Delta H_A^f}{\overline{S}_A^{m,l} - \overline{S}_A^{m,\alpha} + \Delta S_A^f} \qquad [7\text{-}11]$$

As before, expressions for specific solution models are substituted into [7-11], resulting in the following liquidus equations:

(1) **Ideal Solution:** substituting [6-27] and [6-28],

$$T = \frac{\Delta H_A^f}{-R\ln(X_A^l) + R\ln(X_A^\alpha) + \Delta S_A^f} \qquad [7\text{-}12]$$

(2) **Regular Solution:** substituting [6-39] and [6-42],

$$T = \frac{\Omega^l(1 - X_A^l)^2 - \Omega^\alpha(1 - X_A^\alpha)^2 + \Delta H_A^f}{-R\ln(X_A^l) + R\ln(X_A^\alpha) + \Delta S_A^f} \qquad [7\text{-}13]$$

Example Problem 7-5
Assuming Ag-Cu solid and liquid solutions are regular, calculate the parameters Ω^l and Ω^α from analysis of the Ag-Cu phase diagram in Appendix E, Figure E.7.

Solution
From Figure E.7, two sets of data points are tabulated as follows:
$$T = 1201 \text{ K}, \ X_{Cu}^l \approx 0.78, \ X_{Cu}^\alpha \approx 0.96;$$

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* An expression similar to [7-1] can be derived assuming $\Delta C_p \neq 0$.

$$T = 1052 \text{ K}, \quad X_{Cu}^l \approx 0.40, \quad X_{Cu}^\alpha \approx 0.94.$$

Substituting these values and $\Delta H_{Cu}^f = 12{,}972$ J/mol from Table A.2 into [7-13], simultaneous equations are solved for Ω^l and Ω^α:

$$1201 = \frac{\Omega^l(1-0.78)^2 - \Omega^\alpha(1-0.96)^2 + 12{,}972}{8.3144 \ln(0.96/0.78) + 9.566};$$

$$1052 = \frac{\Omega^l(1-0.40)^2 - \Omega^\alpha(1-0.94)^2 + 12{,}972}{8.3144 \ln(0.94/0.40) + 9.566}.$$

Hence,
$$\Omega^l = \underline{12{,}889} \text{ J/mol}, \quad \overline{H}_{Cu}^{m,l} = 12{,}889(1 - X_{Cu}^l)^2;$$

$$\Omega^\alpha = \underline{21{,}111} \text{ J/mol}, \quad \overline{H}_{Cu}^{m,\alpha} = 21{,}111(1 - X_{Cu}^\alpha)^2.$$

As mentioned in Section 6.4, the regular solution model is ideal with respect to entropy, hence from Section 6.5, $\overline{S}_{Cu}^{XS} = 0$. Ω is independent of temperature and composition. A comparison of $\overline{H}_{Cu}^{m,l}$ computed above with data from the literature is given in Table 7.4. Considering the errors inherent in parameters calculated from phase diagrams (Kubaschewski and Alcock, 1979, p. 50-52) and the assumptions listed above, the results are comparable. In addition, the same authors report an excess entropy contribution which suggests that the solution is not strictly regular.

Table 7.4

Calculated $\overline{H}_{Cu}^{m,l}$ Versus Published $\overline{H}_{Cu}^{m,l}$

Ag-Cu Phase Diagram

Source*		$X_{Cu}^l = 0.5$	$X_{Cu}^l = 0.7$	$X_{Cu}^l = 0.9$
K & A:	$\overline{H}_{Cu}^{m,l}$ (J/mol)	3766	1435	159
(1423 K)				
Calculated:	$\overline{H}_{Cu}^{m,l}$ (J/mol)	3222	1160	129
(1050–1200 K)				

* K & A: Kubaschewski and Alcock, 1979, p. 387.
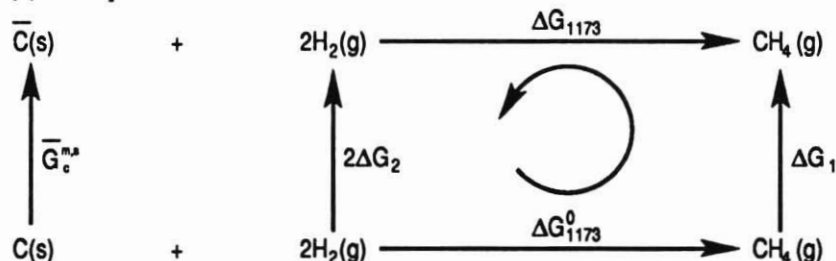
Example Problem 7-6

During *gas-carburizing*, steel parts are placed in a furnace with an atmosphere containing hydrocarbon gases such as methane (CH_4) (Smith 1986, p. 153-158). Carbon diffuses into the surface of the steel and subsequent heat treatment results in a product with a wear-resistant high-carbon case.

Suppose a low carbon steel is carburized at 900°C in a hydrogen-methane mixture. The surface carbon content required is eutectoid in composition or approximately 0.8 w/o.

(a) Calculate the *carburizing potential* $P_{CH_4}/P_{H_2}^2$ required to develop the necessary surface carbon. Note: $\overline{C}(s)$ is carbon dissolved in austenite.

Solution

(1) Set Up.

$$\overline{C}(s) \quad + \quad 2H_2(g) \xrightarrow{\quad \Delta G_{1173} \quad} CH_4(g)$$

$$C(s) \quad + \quad 2H_2(g) \xrightarrow{\quad \Delta G^0_{1173} \quad} CH_4(g)$$

with vertical arrows labeled $\overline{G}_c^{m,s}$, $2\Delta G_2$, and ΔG_1, and a loop labeled ΔG_{1173} (top) and ΔG^0_{1173} (bottom).

(2) Sum.

$$\Sigma \Delta G_{TL} = 0 = \Delta G^0_{1173} + \Delta G_1 - \Delta G_{1173} - 2\Delta G_2 - \overline{G}_C^{m,s}.$$

(3) Substitute. From Table A.4,

$$\Delta G^0_{1173} = -69,126 + 51.26T \log(T) - 65.36T$$
$$= -69,126 + 51.26(1173)\log(1173) - 65.36(1173)$$
$$= 38,757 \text{ J/mol.}$$

$\Delta G_1 = RT \ln(P_{CH_4})$ and $2\Delta G_2 = 2RT \ln(P_{H_2}) = RT \ln(P_{H_2}^2)$.

$\Delta G_{1173} = 0$ (equilibrium).

$\overline{G}_C^{m,s}$ is obtained from Appendix A, Table A.6. The activity of carbon relative to graphite is expressed by the constant temperature conversion a_c (graphite) = a_c (w/o C in austenite)/a_c (w/o C in austenite at saturation). Hence, a_c (0.80 w/o in steel)= 0.048 at 900°C. From the Fe-C phase diagram, the carbon content of saturated austenite at 900°C is 1.18 w/o C. By interpolation between 1.1 and 1.2 w/o C, $a_c = 0.0803$ at 1.18 w/o C.

From [6-14], $\overline{G}_C^{m,s} = 8.3144(1173)\ln(0.0480/0.0803)$. Substituting the above data into $\Sigma \Delta G_{TL} = 0$, $0 = 38,757 + 8.3144(1173) \ln(P_{CH_4}) - 8.3144(1173) \ln(P_{H_2}^2) - 8.3144(1173)\ln(0.0480/0.0803)$.

(4) Solve.

$$P_{CH_4}/P_{H_2}^2 = \underline{0.011}.$$

(b) Assuming $P_{CH_4} + P_{H_2} = 1$ atm, calculate the partial pressure of each gas.

Solution
Solving simultaneously:

From (a) $P_{CH_4} / P_{H_2}^2 = 0.011$;

From (b) $P_{CH_4} + P_{H_2} = 1$ atm.

Hence,

$$P_{H_2}^2 + 90.909\, P_{H_2} - 90.909 = 0,$$

$$P_{H_2} = \{-90.909 + [(90.909)^2 - 4(-90.909)]^{1/2}\}/2 \quad \text{or}$$

$$P_{H_2} = \underline{0.989 \text{ atm}}; \quad P_{CH_4} = 1 - 0.989 = \underline{0.011 \text{ atm}}.$$

Note that excess CH_4 ($P_{CH_4} > 0.011$ atm) drives the reaction from right to left, hence CH_4 is a *carburizing gas*. Conversely, excess H_2 ($P_{H_2} > 0.989$ atm) drives the reaction from left to right, hence H_2 is a *decarburizing gas*.

7.3 CHEMICAL POTENTIAL: PHASES AT EQUILIBRIUM

Referring to Figure 7.4, the ends of the tie-line through point X connect co-existing terminal solid solution phases α and β. The total Gibbs free energy change of the *system* can be found by substituting [4-25], [4-26], and [6-66] into [6-64]:
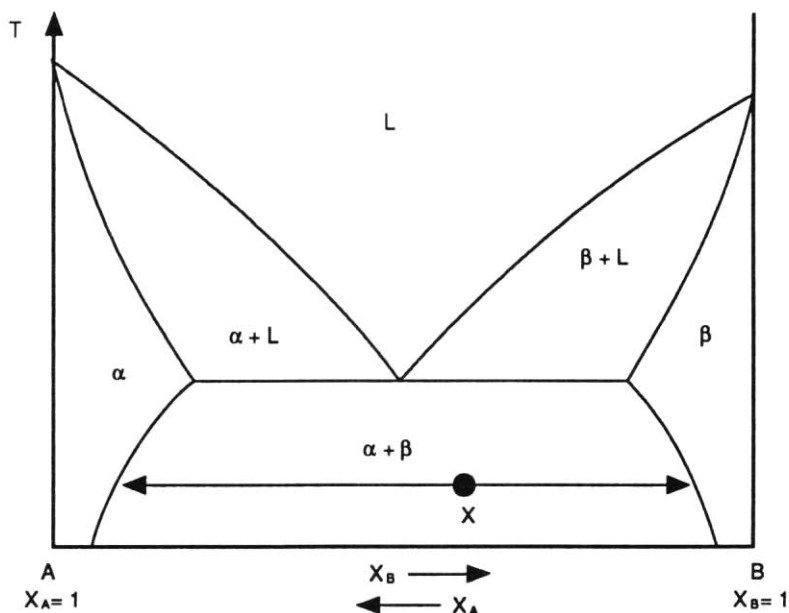

Figure 7.4 Temperature-composition eutectic phase diagram for components A and B with terminal solid solubility. Point X is a composition in the two phase $\alpha + \beta$ field.

$$dG' = dG'_\alpha + dG'_\beta$$
$$= -S'_\alpha dT + V'_\alpha dP + \mu^\alpha_A dn^\alpha_A + \mu^\alpha_B dn^\alpha_B - S'_\beta dT + V'_\beta dP + \mu^\beta_A dn^\beta_A + \mu^\beta_B dn^\beta_B$$

where μ^α_A and dn^α_A are the *chemical potential* of component A in α phase and the differential of the number of moles of A in α respectively. Definitions with respect to β phase are identical. If α and β are in equilibrium at constant temperature and pressure, $dG' = 0$, hence:

$$\mu^\alpha_A dn^\alpha_A + \mu^\alpha_B dn^\alpha_B + \mu^\beta_A dn^\beta_A + \mu^\beta_B dn^\beta_B = 0 \qquad [7\text{-}14]$$

From a mass balance on A,

$$n^\alpha_A + n^\beta_A = n_A.$$

Since the total number of moles of A is constant, $dn^\alpha_A + dn^\beta_A = dn_A = 0$. Hence, for equilibrium to exist between phases α and β,

$$dn^\alpha_A = -dn^\beta_A.$$

Similarly, $\qquad\qquad\qquad dn^\alpha_B = -dn^\beta_B.$

Substituting these equalities into [7-14],

$$\mu^\alpha_A(-dn^\beta_A) + \mu^\alpha_B(-dn^\beta_B) + \mu^\beta_A dn^\beta_A + \mu^\beta_B dn^\beta_B = 0$$

or

$$(\mu^\alpha_A - \mu^\beta_A)dn^\beta_A + (\mu^\alpha_B - \mu^\beta_B)dn^\beta_B = 0.$$

Regardless of the change in the number of moles in each phase, if equilibrium is to be satisfied,

$$\mu^\alpha_A = \mu^\beta_A \qquad [7\text{-}15]$$

$$\mu^\alpha_B = \mu^\beta_B \qquad [7\text{-}16]$$

[7-15] and [7-16] may be extended to any number of phases (solid, liquid, or gas) at equilibrium.

Example Problem 7-7

Determine the activity coefficient, γ^β_{Cu}, in a high Ag-Cu alloy at 500°C.

Solution

Examination of the Ag-Cu alloy phase diagram in Figure E.7 reveals that equilibrium involves two solvus transformations, α and β, at 500°C. At equilibrium, $\mu^\alpha_{Cu} = \mu^\beta_{Cu}$. Assume: (1) Cu behaves ideally in α phase and Henrian in β phase and (2) the standard state for Cu is pure solid copper. Substituting [6-67] into [7-15], $\overline{G}^\alpha_{Cu} = \overline{G}^\beta_{Cu}$. Subtracting G^0_{Cu}, $\overline{G}^\alpha_{Cu} - G^0_{Cu} = \overline{G}^\beta_{Cu} - G^0_{Cu}$. Substituting G for V in [6-7]:

$$\overline{G}^{m,\alpha}_{Cu} = \overline{G}^{m,\beta}_{Cu}.$$

From [6-14], $\qquad\qquad RT\ln(a^\alpha_{Cu}) = RT\ln(a^\beta_{Cu}),$

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$$a_{Cu}^{\alpha} = a_{Cu}^{\beta};$$

$$X_{Cu}^{\alpha} = \gamma_{Cu}^{\beta} X_{Cu}^{\beta}.$$

From the phase diagram at 500°C, the terminal solubility of Ag in α is $\approx$ 2 w/o and the terminal solubility of Ag in β is $\approx$ 98 w/o. Converting to a/o:

2 w/o Ag = 1.19 a/o Ag = 98.81 a/o Cu in α;
98 w/o Ag = 95.65 a/o Ag = 3.35 a/o Cu in β.

Hence, $\qquad X_{Cu}^{\alpha} = \gamma_{Cu}^{\beta} X_{Cu}^{\beta} \Rightarrow 0.9881 = \gamma_{Cu}^{\beta}(0.0335)$

or $\qquad\qquad \gamma_{Cu}^{\beta} = \underline{29.5}.$

As in previous problems, oxidation, sulfidizing, or chloridizing *potential* (gas composition ratios) can be determined for alloyed components if activities in the alloy are obtained from the literature or calculated by first determining γ as described above.

Example Problem 7-8

Develop an expression relating temperature to composition in the two phase $\alpha + \beta$ field of the Ag-Cu system.

Solution

At a temperature slightly below the eutectic, solid compositions are defined by α and β solvus boundaries as shown in Figure 7.5.
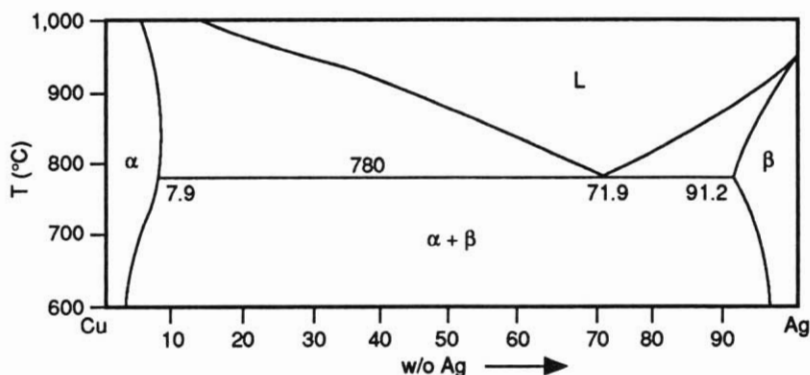

Figure 7.5 Partial Ag-Cu phase diagram at and below the eutectic temperature.

At equilibrium in the two phase field, assuming a standard state of pure solid copper,

$$\overline{G}_{Cu}^{m,\alpha} = \overline{G}_{Cu}^{m,\beta} \text{ where } \overline{G}_{Cu}^{\alpha} = \mu_{Cu}^{\alpha} \text{ and } \overline{G}_{Cu}^{\beta} = \mu_{Cu}^{\beta}$$

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Hence,

$$\overline{H}_{Cu}^{m,\alpha} - T\overline{S}_{Cu}^{m,\alpha} = \overline{H}_{Cu}^{m,\beta} - T\overline{S}_{Cu}^{m,\beta} \ .$$

Solving for T,

$$T = \frac{\overline{H}_{Cu}^{m,\alpha} - \overline{H}_{Cu}^{m,\beta}}{\overline{S}_{Cu}^{m,\alpha} - \overline{S}_{Cu}^{m,\beta}}$$ [7-17]

In Example Problem 7-7, it was assumed that Cu is ideal in α phase and Henrian in β phase at 500°C. If it is assumed, rather, that both solutions are regular with respect to Cu at higher concentrations near 780°C, [7-17] becomes

$$T = \frac{\Omega^\alpha (1 - X_{Cu}^\alpha)^2 - \Omega^\beta (1 - X_{Cu}^\beta)^2}{R \ln(X_{Cu}^\beta / X_{Cu}^\alpha)} \ .$$

Since $\Omega^\alpha = 21,111$ J/mol from Example Problem 7-5, the solution becomes one of finding Ω^β and substituting it back into the above equation. At the eutectic temperature,

$$1053 = \frac{21,111(1 - 0.952)^2 - \Omega^\beta (1 - 0.141)^2}{8.3144 \ln(0.141/0.952)} \ .$$

Hence, $\Omega^\beta = 22,720$ J/mol. The expression for T becomes:

$$T = \frac{21,111(1 - X_{Cu}^\alpha)^2 - 22,720(1 - X_{Cu}^\beta)^2}{R \ln(X_{Cu}^\beta / X_{Cu}^\alpha)} \ .$$

An alternate method of finding Ω^β would be analysis of the Ag liquidus/solidus as is done for the Cu liquidus/solidus in Example Problem 7-5.

7.4 UNIVARIANT EQUILIBRIUM: CLAPEYRON EQUATION

The functional dependence between pressure and temperature for univariant equilibrium can be expressed in terms of the *Clapeyron equation* derived below. For example, consider the *liquid-vapor* transformation for pure component A:

$$A(l) \rightarrow A(g) \qquad \Delta G = G_{A(g)} - G_{A(l)}.$$

From [4-14],

$$dG_{A(l)} = V_{A(l)}dP - S_{A(l)}dT;$$
$$dG_{A(g)} = V_{A(g)}dP - S_{A(g)}dT.$$

At equilibrium,

$$dG_{A(l)} = dG_{A(g)} \text{ hence,}$$
$$V_{A(l)}dP - S_{A(l)}dT = V_{A(g)}dP - S_{A(g)}dT;$$
$$[S_{A(g)} - S_{A(l)}]dT = [V_{A(g)} - V_{A(l)}]dP$$

or

$$dP = \left(\frac{S_{A(g)} - S_{A(l)}}{V_{A(g)} - V_{A(l)}} \right) dT$$ [7-18]

Since the reaction proceeds at constant temperature and pressure, [3-9] substituted into [7-18] gives

$$dP = \frac{\left[H_{A(g)} - H_{A(l)}\right]dT}{\left[V_{A(g)} - V_{A(l)}\right] T} \approx \frac{\left[H_{A(g)} - H_{A(l)}\right]dT}{TV_{A(g)}} \qquad [7\text{-}19]$$

where $V_{A(g)} \gg V_{A(l)}$; $V_{A(g)} - V_{A(l)} \approx V_{A(g)}$. [7-19] is one form of the *Clapeyron equation*. Assuming ideal gas behavior, [1-1] substituted into [7-19] results in an alternate form of the Clapeyron equation sometimes referred to as the *Clausius-Clapeyron equation*:
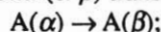
$$\frac{dP}{P} = \frac{\left[H_{A(g)} - H_{A(l)}\right]dT}{RT^2}$$

or

$$\frac{dP}{P} = \frac{\Delta H^V dT}{RT^2} \qquad [7\text{-}20]$$

where ΔH^V is the molar heat of vaporization. For a *solid-vapor* transformation, "*l*" for liquid in [7-18] and [7-19] is replaced by "*s*" for solid, and ΔH^V in [7-20] is replaced by ΔH^s for molar heat of sublimation.

For a *liquid-solid* or *solid-solid* (α-β) transformation,
$$A(\alpha) \rightarrow A(\beta);$$

$$dP = \frac{\left[H_{A(\beta)} - H_{A(\alpha)}\right]dT}{\left[V_{A(\beta)} - V_{A(\alpha)}\right]T} = \frac{\Delta H^{Tr} dT}{T\Delta V} \qquad [7\text{-}21]$$

where ΔH^{Tr} and ΔV denote the molar enthalpy and volume of transformation respectively. ΔH^{Tr} and ΔV may be assumed constant over small temperature intervals to simplify integration of [7-21].

7.5 PRESSURE EFFECT ON PHASE BOUNDARIES

Consider a simple eutectic system with no solid solubility. The effect of pressure on the liquidus will now be estimated. From [4-32] at constant temperature,

$$dH = V(1 - \alpha T)dP \qquad [7\text{-}22]$$

Substituting [1-2] into [4-23],

$$dS = -\alpha V dP \qquad [7\text{-}23]$$

where $(\partial V / \partial T)_P = \alpha V$.

Since α is a thermodynamic property, $\overline{\alpha}_A^{m,l}$ is defined as a partial molar mixing property. Substituting the pressure correction terms $\alpha_A^{o,l}$, $V_A^{o,l}$, $\overline{\alpha}_A^{m,l}$, $\overline{V}_A^{m,l}$, [7-22], and [7-23] into [7-2] ,

$$T = \frac{\overline{H}_A^{m,l} + \int_{P_1}^{P_2} \overline{V}_A^{m,l}(1 - \overline{\alpha}_A^{m,l}T)dP + \Delta H_A^f + \int_{P_1}^{P_2} V_A^{0,l}(1 - \alpha_A^{0,l}T)dP}{\overline{S}_A^{m,l} - \int_{P_1}^{P_2} \overline{V}_A^{m,l}\overline{\alpha}_A^{m,l}dP + \Delta S_A^f - \int_{P_1}^{P_2} V_A^{0,l}\alpha_A^{0,l}dP} \qquad [7\text{-}24a]$$

The above equation is simplified in the numerator by neglecting αT terms since $\overline{\alpha}_A^{m,l}T \approx \alpha_A^{0,l}T \ll 1$. In the denominator, $\overline{V}_A^{m,l}\overline{\alpha}_A^{m,l} \approx V_A^{0,l}\alpha_A^{0,l} \ll (\overline{S}_A^{m,l} + \Delta S_A^f)$. Assuming $\overline{V}_A^l \approx V_A^{0,l}$ and $V_A^{0,l}$ is independent of pressure, the above equation reduces to

$$T = \frac{\overline{H}_A^{m,l} + V_A^{0,l}(P_2 - P_1) + \Delta H_A^f}{\overline{S}_A^m + \Delta S_A^f} \qquad [7\text{-}24b]$$

Example Problem 7-9

Predict the liquidus temperature shift caused by increasing the hydrostatic pressure from 1 to 1000 atm over a 60 a/o Si-Al alloy.

Solution

From Example Problem 7-1, $\Delta H_{Si}^f = 50,630$ J/mol, $\overline{H}_{Si}^{m,l} = -12,267(1 - X_{Si})^2$ and $\Delta S_{Si}^f = 50,630/1693 = 29.91$ J/(mol·K). From Table B.1, $V_{Si}^{0,l} = M_{Si} / \rho_{Si}$ $= 28.09/2.57 = 10.93$ cm^3/mol. Substituting into [7-24b],

$$T = \frac{-12,267(1 - 0.6)^2 + (10.93)(999)(0.101) + 50,630}{-8.3144 \ln(0.6) + 29.91}$$

$$= \frac{49,770}{34.16} = 1457 \text{ K.}$$

Since the liquidus temperature is ≈ 1424 K at $X_{Si} = 0.6$ and 1 atm, the liquidus shifts upward by approximately 33 K. In a high Al-Si solution, Wu (1992, p. 1-5) predicted an upward shift of ≈ 50 K for an increase in pressure from 1 to 6800 atm. The above assumptions become less valid at higher pressures.

Example Problem 7-10

Develop an expression that predicts the effect of pressure on solvus boundaries in the $\alpha + \beta$ region of Figure 7.3.

Solution

Starting with [7-17], incorporate pressure correction terms corresponding to those used to develop [7-24a]:

$$T = \frac{\overline{H}_A^{m,\alpha} + \int_{P_1}^{P_2} \overline{V}_A^{m,\alpha}(1 - \overline{\alpha}_A^{m,\alpha}T)dP - \overline{H}_A^{m,\beta} - \int_{P_1}^{P_2} \overline{V}_A^{m,\beta}(1 - \overline{\alpha}_A^{m,\beta}T)dP}{\overline{S}_A^{m,\alpha} - \int_{P_1}^{P_2} \overline{V}_A^{m,\alpha}\overline{\alpha}_A^{m,\alpha}dP - \overline{S}_A^{m,\beta} + \int_{P_1}^{P_2} \overline{V}_A^{m,\beta}\overline{\alpha}_A^{m,\beta}dP} \qquad [7\text{-}25a]$$

Assuming $\overline{\alpha}_A^{m,\alpha}T \approx \overline{\alpha}_A^{m,\beta}T \ll 1$, $\nabla_A^{m,\alpha}\overline{\alpha}_A^{m,\alpha} \approx \nabla_A^{m,\beta}\overline{\alpha}_A^{m,\beta} \ll (\overline{S}_A^{m,\alpha} - \overline{S}_A^{m,\beta})$, and that ∇_A^α and $\overline{\nabla}_A^\beta$ are independent of pressure,

$$T = \frac{\overline{H}_A^{m,\alpha} + (\nabla_A^\alpha - \nabla_A^\beta)(P_2 - P_1) - \overline{H}_A^{m,\beta}}{\overline{S}_A^{m,\alpha} - \overline{S}_A^{m,\beta}}$$ [7-25b]

7.6 GIBBS PHASE RULE

A discussion of phase equilibrium is not complete unless the concept of the *Gibbs phase rule* is introduced. A simple way to visualize the concept is to consider it analogous to the simultaneous solution of a set of mathematical equations. A three variable set, for example, requires three equations if the values of the three variables are to be determined. If only two equations or relationships are known between the three variables, the set can be solved by fixing one of the variables. Simultaneous solution of a two variable-two equation set can then be accomplished. The choice or arbitrary selection of *one* of the variables, in terms of the phase rule concept, means that there is one degree of *freedom* or *variance*, F. The concept is formalized by

$F = $ [Number of variables] $-$ [Number of equations]   [7-26]

For two equations in a three variable set, $F = 3 - 2 = 1$ degree of freedom.

The concept can now be applied to point X in the $\alpha + \beta$ region of Figure 7.4. At constant temperature, X_A^α is known thus X_B^α is fixed. Likewise, X_A^β is known thus X_B^β is fixed. As a result, there are two composition variables, one for each phase. A generalized expression for the number of composition variables is

[Number of composition variables] $= \phi(\Gamma - 1)$ [7-27]

where ϕ is the number of phases and Γ is the number of components in the system. Using [7-27], [Number of composition variables] $= 2(2 - 1) = 2$, which is in agreement with the above at point X.

The number of equations that prevail must now be established. From [7-15] and [7-16], the chemical potential of each component is the same in each phase at equilibrium. This leads to two equations. A generalized expression for the number of equations is therefore

[Number of equations] $= \Gamma(\phi - 1)$ [7-28]

Using [7-28], [Number of equations] $= 2(2 - 1) = 2$. Substituting [7-27] and [7-28] into [7-26],

$F = \phi(\Gamma - 1) - \Gamma(\phi - 1) = \Gamma - \phi$ [7-29]

Since pressure and temperature are additional variables, a general form of the Gibbs phase rule is

$F = \Gamma - \phi + 2$ [7-30]

Since phase diagrams are normally obtained experimentally at 1 atm pressure, the more common form of [7-30] is

$F = \Gamma(\text{Components}) - \phi(\text{Phases}) + 1$ [7-31]

For point X in Figure 7.4, $F = 2 - 2 + 1 = 1$ degree of freedom. This means if

one variable is fixed (temperature), the other variable (composition of both phases) is detérmined by the diagram. While the example in this discussion applies to a two component system, [7-31] applies in general to multicomponent systems.

7.7 DISCUSSION QUESTIONS

(7.1) Rewrite [7-11] for the case where $\Delta C_p \neq 0$.

(7.2) What is the basis for determining boundaries on phase diagrams by TL analysis? Briefly discuss and illustrate with a sketch.

(7.3) Two phases in equilibrium contain the same chemical component i. Is the concentration of i in each phase the same? Explain.

(7.4) Two Fe-Mg silicate minerals, garnet and pyroxene, are determined to be in chemical equilibrium. What information is needed to relate the Fe and Mg activity coefficients and concentrations in each mineral?

(7.5) Consider Figure 7.3. Does $\Omega^l = \Omega^\alpha = \Omega^\beta$? Discuss.

(7.6) Based on [7-25b], what condition exists if temperature is independent of pressure?

7.8 EXERCISE PROBLEMS

[7.1] Using the Bi-Pb phase diagram in Appendix E, Figure E.8, calculate the activity of Bi in an equimolar liquid solution of Bi and Pb at 625 K. Assume regular solution behavior.

Ans: $a_{Bi} = 0.38$.

[7.2] Using the results from Exercise Problem [7.1], calculate the equilibrium $P_{O_2(g)}$ over an equimolar Bi-Pb liquid solution at 625 K. The Gibbs free energy of formation of dibismuth trioxide, Bi_2O_3, is $\Delta G^{0,f}_{Bi_2O_3} = -407,250$ J/mol at 625 K (Wicks and Block, 1963, p. 21).

Ans: $P_{O_2(g)} \approx 7.4 \times 10^{-23}$ atm.

[7.3] From Kubaschewski and Alcock (1979), solution data for a 70 a/o Bi-Pb solution (Exercise Problem [7.1]) are: $\overline{H}^{m,l}_{Bi} = -70 \times 4.184 = -292.9$ J/mol and $\overline{S}^{XS}_{Bi} = 0.03 \times 4.184 = 0.1255$ J/(mol·K). Using this data, estimate the heat of fusion of Bi.

Ans: $\Delta H^f_{Bi} = 9507$ J/mol or a 13% error—attributed to reading error from the diagram and the assumption that $\Delta C_p \approx 0$.

[7.4] Repeat Exercise Problem [6.9] using the following solubility data estimated from the Pb-Sb phase diagram in Appendix E, Figure E.9: $X_{Sb} = 0.3$ at T = 598 K and $X_{Sb} = 0.2$ at $T = 533$ K. Note that the solubility data is given at a much lower temperature than the refining temperature. Assume:

(1) Calculated solution parameters hold at the higher temperature,

(2) The process involves the reaction

$$2\overline{Sb} + 3PbO(s) \rightarrow 3\overline{Pb} + Sb_2O_3(s);$$

(3) Sb behaves as a dilute solution component at these concentrations.

Ans: $X_{Sb} \approx 0.011$ or ≈ 6500 ppm Sb. Note: assuming Sb be-

haves ideally (Exercise Problem [6.9]—Method 2) yields a result 23% higher.

[7.5] For dilute solutions of carbon (graphite) in liquid sodium, solubility data was used to determine the partial molar free energy of solution as a function of temperature according to Johnson (1964, p. 23) as follows:

$$\overline{G}_C^l - G_C^{0,S} = 5272 + 68.62T + 8.3144T \ln(X_C).$$

(a) Determine $\overline{H}_C^{XS}$ and $\overline{S}_C^{XS}$.

Ans: $\overline{H}_C^{XS} = h_C = 5272$ J/mol; $\overline{S}_C^{XS} = s_C = -68.62$ J/(mol·K).

(b) The purification of liquid sodium with respect to carbon can be accomplished by *gettering* carbon with calcium at 920°C. Predict the carbon content of the liquid after addition of excess calcium. The solubility of Ca in Na is low, hence, it has no effect on the performance of sodium as a heat transfer medium.

Ans: $X_C = 1.5 \times 10^{-6}$ or ≈0.8 ppm C.

[7.6] Using the following data from Kubaschewski and Alcock (1979, p. 386-389) for Cu in a Ag-Cu liquid alloy at 1423 K:

X_{Cu}	0.0	0.1	0.3	0.5	0.7	0.9
$\overline{H}_{Cu}^{m,l}$ (J/mol)	23,014	15,692	7482	3766	1435	159
$\overline{S}_{Cu}^{XS}$ [J/(mol·K)]	5.980	3.084	0.456	0.100	0.084	0.004

(a) Calculate $\overline{G}_{Cu}^{XS}$.

Ans:

X_{Cu}	0.0	0.1	0.3	0.5	0.7	0.9
$\overline{G}_{Cu}^{XS}$ (J/mol)	14,504	11,303	6833	3624	1315	153.3

(b) Calculate $\overline{G}_{Cu}^{XS}$ from the results in Example Problem 7-5 and compare with part (a).

Ans:

X_{Cu}	0.0	0.1	0.3	0.5	0.7	0.9
$\overline{G}_{Cu}^{XS}$ (J/mol)	12,889	10,440	6316	3222	1160	129

These results differ from those of part (a) by 11-16%. See Example Problem 7-5 for further discussion.

[7.7] Using the data from Example Problem 7-8 and Appendix B, Table B.1, predict the eutectic temperature shift resulting from a pressure increase from 1 to 1000 atm.

Ans: From Appendix E, Figure E.7, $T_e = 1053$ K. The eutectic temperature shift is a maximum of + 20 K. In reality, the shift is less—depending upon the actual value of $\overline{V}_{Cu}^{\beta}$.

[7.8] Refer to the eutectic phase diagram shown in Appendix E, Figure E.10.
   (a) Identify the components that constitute this system.
      Ans: $NaAlSi_3O_8$ and SiO_2.
   (b) Is the system isobaric or isothermal?
      Ans: Isobaric.
   (c) Give the phase rule expression that is applicable to this diagram.
      Ans: $F = \Gamma - \phi + 1$, pressure is constant.
   (d) Label the diagram at phase assemblages which are: *invariant* ($F = 0$), *univariant* ($F = 1$), and *divariant* ($F = 2$).
   (e) What is the equation (temperature) of the horizontal line through the eutectic point?
      Ans: $T \approx 1060°C$.
   (f) What is the equation (temperature) of the phase boundary between tridymite and cristobalite?
      Ans: $T \approx 1470°C$.

[7.9] Using Figure E.11 in Appendix E, develop a temperature-dependent expression for the diamond-graphite phase boundary between 45–105 kbar. Is this boundary invariant, univariant, or divariant? See Exercise Problem [7.8].
      Ans: $P(kbar) = 0.029 \times T(K) + 7$, univariant ($F = 1$).

[7.10] Estimate the equilibrium vapor pressure of $SO_2(g)$ over $SO_2(l)$ at 265 K. State assumptions.
      Ans: $P_{SO_2(g)} = 1.09$ atm, ΔH^{Tr} is assumed constant.

[7.11] Estimate the solid-liquid isothermal transformation temperature of Au at 75 atm. State assumptions.
      Ans: $T_{75\ atm} = 1337$ K, ΔH^{Tr} and ΔV^{Tr} are assumed constant.